

DESCRIPTION

CELL AND POWER GENERATION METHOD

Technical Field

The present invention relates to a cell and a method of power generation using the same. More particularly, the present invention relates to a cell and a method of power generation making use of an acidic medium and a basic medium being kept into contact with the acidic medium (i.e., a bipolar-type reaction field).

Background Art

A cell is a device that converts chemical energy of a substance directly into electric energy. Further, cells can be classified into primary cells that discharge electric power until their chemical energy is used up, secondary cells capable of being reused by storing chemical energy again by a charging operation after being used up, and fuel cells that obtain electric energy by continually being supplied with a substance having chemical energy from outside. Currently, numerous-types of cells have been developed. Each cell has different advantages and disadvantages with respect to each item of environmental safety, economy, amount of electric energy that can be supplied, portability, storage properties, adaptation to an environment of use, recycling performance, and the like, so that cells are selected and put to practical use in accordance with an intended use. Critical technical factors that are common to all cells are what chemical substances are used for

reaction, how the reaction is promoted, and in what form the chemical substances are stored, supplied and collected.

A cell makes use of two kinds of chemical substances, namely, a reducing agent that causes a reduction reaction (donating electrons to the opposing party or drawing oxygen therefrom) and an oxidizing agent that causes an oxidation reaction (drawing electrons from the opposing party or giving oxygen thereto). By causing these reactions separately at two electrodes that oppose each other, the energy of generated electrons is taken to the outside (ions produced at the two electrodes accompanying the generation of electrons are neutralized within the cell). Reaction efficiency depends on the kind and reaction style of the chemical substances to be used, material and activity of electrodes, and the environment of reaction fields including electrolytes. Further, what substances are to be selected to constitute a cell is a point affecting whether the whole cell system will be good or bad not only at the time of use but also at the time of manufacturing and at the time of discarding after use.

For example, manganese system or mercury system primary cells are excellent in economical efficiency and storage properties of the chemical substances. However, when harmful heavy metals are let alone after using the manganese system or mercury system primary cells, it adversely affects the environment, so that they must be collected strictly. Since the manganese system or mercury system primary cells cannot be reused by self-charging, problems are caused in that discarding of cells after use and reuse of resources are expensive.

For example, lithium ion secondary cells are sufficient in the amount of electrical

energy, and can be reused by self-charging. However, lithium is an extremely unstable flammable dangerous substance with respect to water or oxygen in the air. For this reason, in order to prevent such danger, sufficient safety countermeasures should be taken for packaging the cells or for protecting the environment at the time of use of the cells. Collection and reuse of the resource of the cells after expiration are also essential thus boosting the entire cost for implementing the processes of manufacturing, using, and discarding the cells. The same problem may occur in lead system storage cells, and from manufacturing cost and electric energy supply points of view, status quo is such that a large amount of the lithium ion system secondary cells is used for vehicle batteries or the like.

On the other hand, among fuel cells, cells are mainly known in which hydrogen or methanol is used as a reducing agent (fuel) or oxygen or hydrogen peroxide is used as an oxidizing agent. For example, so-called direct methanol cells have been proposed in which methanol is used as a reducing agent (fuel) and an aqueous solution of hydrogen peroxide is used as an oxidizing agent (see U.S.P No. 6, 485, 851, for example).

In the case of these cells, since methanol and an aqueous solution of hydrogen peroxide are in a liquid state at an ordinary temperature and under a normal pressure, they are excellent in portability or storage properties. However, there is a critical problem in that the cells produce carbon dioxide which is a substance that causes green house phenomenon to occur accompanying the reaction and imposes burden on the environment. Further, methanol as a fuel is flammable, so that its leakage results in a serious danger. Moreover, problems are still arisen in that use of a large amount of noble metal reaction catalyst for causing reactions makes the manufacturing cost higher, methanol fuel at the

side of a cathode moves, through a solid electrolyte film, to the side of an anode, and methanol crossover may occur thus deteriorating reaction efficiency.

Further, hydrogen-oxygen system fuel cells can supply a large amount of electric energy and produces only water as a reaction product, so that the hydrogen-oxygen system fuel cells are extremely excellent in environmental safety. However, hydrogen as a fuel is flammable, so that its leakage results in a serious danger.

Moreover, the cited document (see Electrochemistry 71, No. 5 (2003) 313-317) discloses a cell of a bipolar-type, as a hydrogen-oxygen fuel cell, in which a strong acidic high polymer membrane is provided at an anode (negative electrode) side and a strong basic high polymer membrane is provided at a cathode (positive electrode) side. Further, the cited document also described that the fuel cells have such advantages that oxidization reaction which is a rate reaction at the anode is initiated comparatively well, and electrode catalysts have high option, and water produced by the reaction is hard to affect the electrodes, and the like.

By the way, in the bipolar-type cells, a reduction reaction is provoked at the side of a strong acidic high polymer membrane, and an oxidation reaction is provoked at the side of a strong basic high polymer membrane. However, the bipolar-type cells are structured such that potentials due to the neutralization of hydrogen ions H^+ and hydroxide ions OH^- at the center of the cells occupy a larger part of the electromotive force than the electromotive force due to the oxidation and reduction reactions of the bipolar-type cells. This is because the potential due to the neutralization of hydrogen ions H^+ and hydroxide ions OH^- is generally higher than one due to other ions.

For this reason, the electromotive properties of this-type of the bipolar-type cell depend on the neutralizing reaction of water produced in the vicinity of a border between the acidic high polymer membrane and the basic high polymer membrane. However, a region where hydrogen ions H^+ and hydroxide ions OH^- come across cannot be a border portion between both high polymer membranes, and is actually dispersed into a wide region where the border is principally located. Further, water produced in accompanying with the neutralization makes it difficult to move hydrogen ions H^+ and hydroxide ions OH^- . Accordingly, since the site where the neutralizing reaction of hydrogen ions H^+ and hydroxide ions OH^- is actually taken place tends to fluctuate, the bipolar-type cell of this-type has a property of having difficulty in generating electromotive force stably.

Further, water produced in this bipolar-type cell has a possibility of being accumulated into the interface between both high polymer membranes to form a water layer. The existence of the water layer may hinder the neutralization reaction between hydrogen ions H^+ and hydroxide ions OH^- thereby resulting in difficulty in supplying electric energy in accordance with the formation or the increase of water layer with time.

Accordingly, an object of the present invention is to provide a bipolar-type cell which is a cell having a novel structure which is able to generate power stably, and a method of power generation using the same.

According to some aspects of the present invention, one object of the present invention is to provide a novel cell for meeting various needs, and solving various problems, which have been caused by the conventional cells, such as occurrence of danger due to the use of flammable and ignitable fuels, discharge of carbon dioxide, complicated storage

properties, and a complicated structure of the cell.

Disclosure of the Invention

The above-described problems can be solved by the inventions as follows:

A cell of the present invention comprises an acidic medium, a first electrode which is disposed in the acidic medium, a basic medium which is kept in contact with the acidic medium, and a second electrode which is disposed in the basic medium,

wherein the acidic medium contains a first substance which causes a reaction of removing electrons from the first electrode, accompanied by hydrogen ions contained therein, and the basic medium contains a second substance which causes a reaction of donating electrons to the second electrode, accompanied by hydroxide ions contained therein.

In accordance with the cell of the present invention, when hydrogen ions H^+ and hydroxide ions OH^- are involved in the reaction at the electrodes, the first substance in the acidic medium, accompanied by the hydrogen ions H^+ in the acidic medium, causes an oxidation reaction that removes electrons from the first electrode, and the second substance in the basic medium, accompanied by the hydroxide ions OH^- in the basic medium, causes a reduction reaction that donates electrons to the second electrode. At this time, the electromotive force by oxidation reaction in an acidic medium becomes, in principle, larger than the electromotive force by oxidation reaction generated in a basic medium. This is due to the following reason. Since hydrogen ions H^+ are a substance of the reactant, the chemical equilibrium tends to be shifted to the product in an acidic medium having a high

hydrogen ion concentration, thereby raising the oxidation potential. Also, the electromotive force by reduction reaction generated in a basic medium becomes, in principle, larger than the electromotive force by reduction reaction generated in an acidic medium. This is due to the following reason. Since hydroxide ions OH^- are a substance of the reactant, the chemical equilibrium tends to be shifted to the product in a basic medium having a high hydroxide ion concentration, thereby lowering the oxidation potential.

For this reason, according to the structure of the bipolar-type cell of the invention, the electromotive force generated by the oxidation-reduction reaction at the electrodes is a principal source of the voltage obtained from the cell, so that the cell of the invention can generate electric power more stably than a different bipolar-type cell in which the electromotive force is generated principally in an area having a property such that the site where the neutralizing reaction is generated within the cell tends to fluctuate as described in the aforementioned non-patent document 2.

Further, a method of power generation by using a cell comprises an acidic medium, a first electrode which is disposed in the acidic medium, a basic medium being kept into contact with the acidic medium, and a second electrode which is disposed in the basic medium,

wherein a first substance which is contained in the acidic medium causes a reaction of removing electrons from the first electrode, accompanied by hydrogen ions contained therein, and a second substance which is contained in the basic medium causes a reaction of donating electrons to the second electrode, accompanied by hydroxide ions contained

therein.

In accordance with a method of power generation of the present invention, as described above, the electromotive force due to the oxidation and reduction reactions at the electrodes can be a subjective source of a voltage that can be obtained from the cell. Consequently, a power force can be generated more stably.

Brief Description of the Drawings

Fig. 1 is a view illustrating a power generation mechanism (method of power generation) using a cell of the present invention;

Fig. 2A is a schematic perspective view of a top surface of a chip-type fluid fuel cell according to a first embodiment of the present invention;

Fig. 2B is a cross-sectional view of the chip-type fluid fuel cell in Fig. 2A, taken along a line A-A', as seen from directions in which both media flow.

Fig. 3A is a schematic cross-sectional perspective view of a paper-type fuel cell according to the first embodiment of the present invention;

Fig. 3B is a schematic cross-sectional perspective view of a paper-type fuel cell according to the first embodiment of the present invention;

Fig. 4 is a schematic cross-sectional perspective view of a gel-type primary cell according to the first embodiment of the present invention;

Fig. 5 is a graph showing the results of current-voltage characteristics in Example using the chip-type fluid fuel cell; and

Fig. 6 is a graph showing the results of current-voltage characteristics in Example

using the paper-type fluid fuel cell.

Best Mode for Carrying Out the Invention

Hereinafter, a detailed description of the present invention will be made.

<Cells>

The cell of the present invention comprises an acidic medium, a first electrode which is disposed in the acidic medium, a basic medium which is kept in contact with the acidic medium, and a second electrode which is disposed in the basic medium,

wherein the acidic medium contains a first substance which causes a reaction of removing electrons from the first electrode, accompanied by hydrogen ions contained in the acidic medium, and the basic medium contains a second substance which causes a reaction of donating electrons to the second electrode, accompanied by hydroxide ions contained in the basic medium.

The cell of the invention is a primary cell of bipolar-type having a structure equipped with the above-described members, and can be used for any-type of a primary cell, a secondary cell, or a fuel cell.

Further, in the invention, the bipolar-type cell refers to a cell having a structure such that the acidic medium and the basic medium are disposed adjacent to each other, and these include a substance for taking out electric energy and electrodes.

In particular, in the bipolar-type cell of the invention, (1) the first substance and hydrogen ions coexist in the acidic medium or near the electrode which is kept in contact

therewith, and together cause a reaction (oxidation) of removing electrons from the first electrode as reactant substances. Further, (2) the second substance and hydroxide ions coexist in the aforementioned basic medium or near the electrode which is in contact therewith, and together cause a reaction (reduction) of donating electrons to the second electrode as reactant substances. Such reactions of (1) and (2) proceed simultaneously to generate the electric energy that drives an outside circuit.

Here, in the cell of the invention in a bipolar-type reaction field, the hydrogen ions constituting a part of the acidic medium participate in the reaction of removing electrons from the first electrode by the first substance, and the increase in the concentration thereof performs a function of promoting the reaction (shifting the chemical equilibrium in the direction of the product). On the other hand, the hydroxide ions constituting a part of the basic medium participate in the reaction of donating electrons to the second electrode by the second substance, and the increase in the concentration thereof performs a function of promoting the reaction (shifting the chemical equilibrium in the direction of the product). For this reason, the reaction can be reinforced by raising the hydrogen ion concentration or the hydroxide ion concentration, i.e. by lowering the pH in the acidic medium and raising the pH in the basic medium, so that the cell is effective in terms of having a structure that can increase the output.

Hereinafter, each member of the cell of the invention will be described in detail.

(Acidic medium and Basic medium)

In the invention, the acidic medium refers to a medium having a pH of 7 or less, and

is preferably capable of forming an acidic reaction field. Further, the basic medium refers to a medium having a pH of more than 7 and is preferably capable of forming a basic reaction field.

Although these acidic medium and basic medium may have any aspect of being in a state of liquid, gel or solid, both media preferably have the same aspect. Further, these acidic medium and basic medium can be used irrespective of whether they are organic compounds or inorganic compounds.

Preferable examples of combinations of the acidic medium and the basic medium include combinations of an acidic aqueous solution such as sulfuric acid, hydrochloric acid or phosphoric acid with a basic aqueous solution such as sodium hydroxide, potassium hydroxide, ammonia or ammonium compounds; a combination of ion conductive gels in which these aqueous solutions gelated by a gelling agent; a combination of an acidic ion exchange member (including a form such as a membrane or filter paper using ion exchange resin) having a sulfonic acid group or a phosphoric acid group with a basic ion exchange member having a quaternary ammonium group; and a combination of solid substances such as a combination of a solid super acid such as zirconia oxide treated with sulfuric acid or zirconia oxide containing a noble metal and a solid acid with a solid super base such as barium oxide and a solid base.

More specifically, the acidic aqueous solution preferably includes one or more acids selected from a group consisting of sulfuric acid, methanesulfonic acid, trifluoromethanesulfonic acid, hydrochloric acid, hydriodic acid, hydrobromic acid, perchloric acid, periodic acid, orthophosphoric acid, polyphosphoric acid, nitric acid,

tetrafluoroboric acid, hexafluorophosphoric acid, hexafluoroarsenic acid, hexachloroplatinic acid, acetic acid, trifluoro acetic acid, citric acid, oxalic acid, salicylic acid, tartaric acid, maleic acid, malonic acid, phthalic acid, fumaric acid, squaric acid, and picric acid. Among these, more preferably, the acidic aqueous solution includes sulfuric acid, hydrochloric acid, nitric acid or phosphoric acid which is a strong acid.

Further, the basic aqueous solution preferably includes one or more bases selected from the group consisting of sodium hydroxide, potassium hydroxide, lithium hydroxide, calcium hydroxide, barium hydroxide, magnesium hydroxide, ammonium hydroxide, tetramethylammonium hydroxide, tetraethylammonium hydroxide, tetrapropylammonium hydroxide, and tetrabutylammonium hydroxide, or includes one or more alkali metal salts of weak acids selected from the group consisting of sodium carbonate, sodium hydrogencarbonate, potassium carbonate, potassium hydrogencarbonate, sodium borate, potassium borate, sodium silicate, potassium silicate, sodium tripolyphosphate, potassium tripolyphosphate, sodium aluminate, and potassium aluminate. More preferably, the basic medium includes sodium hydroxide or potassium hydroxide which is a strong base.

Further, use of an acidic ion conductive gel as an acidic medium is preferable in which the acidic aqueous solution as described above is gelled by using a gelling agent such as water glass, anhydrous silicon dioxide, cross-linked polyacrylic acid or a salt thereof.

On the other hand, use of a basic ion conductive gel as a basic medium is preferable in which the basic aqueous solution is gelled by using a gelling agent such as carboxymethyl cellulose, cross-linked polyacrylic acid or a salt thereof.

Here, the acid or the base may be constituted of one kind or a mixture of two or more kinds selected from the above-described compounds. Also, the way of using the gelling agent is the same as described above.

Further, the aforementioned acidic ion exchange member and basic ion exchange member include a form such as ion exchange membrane, solid polymer electrolyte membrane, or filter paper, using ion exchange resin. Preferable examples thereof include ion exchange members using a strongly acidic ion exchange member having a strong acidic group such as sulfonic acid group or phosphoric acid group or a strongly basic ion exchange member having a strong basic group such as quaternary ammonium group.

More specific examples include polyvinylstyrene ion exchange resins represented by DOWEX (trade name, manufactured by Dow Co., Ltd.), DIAION (trade name, manufactured by Mitsubishi Chemical Co., Ltd.), and AMBERLITE (trade name, manufactured by Rohm and Hass Co., Ltd.), polyfluorohydrocarbon polymer solid polymer electrolyte membranes such as NAFION (trade name, manufactured by DuPont Co., Ltd.), FLEMION (trade name, manufactured by Asahi Glass Co., Ltd.), and ASIPLEX (trade name, manufactured by Asahi Kasei Industry Co., Ltd.), polyvinylstyrene ion exchange membranes such as NEOSEPTA (trade name, manufactured by Tokuyama Co., Ltd.) and NEOSEPTA BP-1 (trade name, manufactured by Tokuyama Co., Ltd.), and ion exchange filter paper formed with polystyrene fibrous ionex ion exchanger such as RX-1 (trade name, manufactured by Toray Co., Ltd.).

Furthermore, preferable examples of solid superacid include zirconia oxide treated with sulfuric acid and zirconia oxide containing a noble metal. In addition, as solid acid,

it is possible to use clay mineral such as kaolinite or montmorillonite, zeolite, composite oxide, hydrated oxide, and activated carbon having an acidic medium deposited thereon.

Preferable examples of solid superbase include barium oxide, strontium oxide, and calcium oxide. In addition, as solid base, it is possible to use metal oxides such as magnesium oxide, and composite oxide containing these, hydroxides having a low solubility to water such as calcium hydroxide, alkali metal or alkali earth metal ion exchange zeolite, and activated carbon having a basic medium deposited thereon.

In the cell of the invention, it is essential that the acidic medium and the basic medium are disposed adjacent to or near each other. This is to make it possible to hold a balance of charge by allowing a salt to be formed with a counter anion generated by release of a hydrogen ion constituting a part of the acidic medium in the acidic medium and a counter cation generated by release of a hydroxide ion constituting a part of the basic medium in the basic medium. For this reason, as described above, if the two media consists of an acidic aqueous solution and a basic aqueous solution, a mode can be employed in which the acidic medium and the basic medium are separated from each other by using a separation membrane having a property of transmitting the generated positive ions and/or negative ions therethrough.

(First substance and second substance)

In the present invention, the first substance can use any substance as long as it is a substance (oxidant) which causes an oxidation reaction that removes electrons from the first electrode, accompanied by hydrogen ions. However, the first substance is preferably

a substance that promotes the reaction when the hydrogen ion concentration is high. Specifically, one can use hydrogen peroxide, oxygen, hypohalogenous acid such as hypochlorous acid, hypobromous acid, or hypoiodous acid, or the like. Further, the first substance may be supplied by using a liquid or a solid that contains these substances, or a liquid or a solid that discharged these substances by a chemical change.

Further, in the present invention, the second substance can use any substance as long as it is a substance (reducing agent) which causes a reduction reaction that donates electrons to the second electrode, accompanied by hydroxide ions. However, the second substance is preferably a substance that promotes the reaction when the hydroxide ion has high concentration. Specifically, one can use hydrogen peroxide, hydrogen, hydrazine, or the like. Here, the second substance may be supplied by using liquid or solid containing theses substances or by using liquid or solid that discharges these substances due to a chemical change.

Further, the first substance or the second substance can use metal ions such as iron, manganese, chromium, and vanadium or their metal complexes which can change the number of valances by the oxidation reaction and the reduction reaction, and can be supplied by using a liquid or a solid containing these.

Among them, the first substance and the second substance are preferably formed by the same component. Such a substance has a property such that, when in an acidic medium, the substance accompanied by hydrogen ions causes an oxidation reaction of removing electrons from the first electrode and, when in a basic medium, the substance accompanied by hydroxide ions causes a reduction reaction of donating electrons to the

second electrode. In this case, the structure of the cell is simple, thereby enlarging the degree of freedom in selecting a separation membrane between chemical substances on the anode side and on the cathode side, which has been a great problem in conventional cells. If the acidic medium and the basic medium can be kept in a non-mixed state, the separation membrane is not necessarily needed.

As the substance that can be used both as the oxidizing agent and the reducing agent, use of hydrogen peroxide is particularly preferable. The reason for this will be described in detail later. Further, in view of handling, it is preferable to supply hydrogen peroxide by using a liquid or a solid that contains therein hydrogen peroxide or by using a liquid or a solid that discharges hydrogen peroxide by a chemical change.

The "liquid" as one of the supplying means of the first substance and the second substance can take any formation of a solution (containing water, organic medium or the like as a solvent), a dispersion solution, or a gel. Further, it is desired to select these formations to be used in a preferable combination with the formations of the acidic medium and the basic medium.

Moreover, in the case of primary cells, both substances are mixed or dispersed into media before the initiation of the reaction. In addition, in the case of fuel cells, they may be previously mixed or dispersed into the media in a liquid state, or they are added to the media, through a channel formed near the electrodes, by being soaked into a capillary, or in a direct manner.

(First electrode and Second electrode)

In the invention, the first electrode is an anode, and the second electrode is a cathode. As materials for the first electrode and second electrode, those similar to those of the electrodes in conventional cells can be used. More specifically, the first electrode (anode) may be made of platinum, platinum black, platinum-oxide-coated platinum, silver, gold, or the like. Further, the first electrode may be made of surface-passivated titanium, stainless steel, nickel, aluminum, or the like. Further, the first electrode may be made of a carbon structure such as graphite or a carbon nanotube, amorphous carbon, glassy carbon, or the like. Here, in view of durability, use of platinum, platinum black, or platinum-oxide-coated platinum is more preferable.

The second electrode (cathode) may be made of platinum, platinum black, platinum-oxide-coated platinum, silver, gold, or the like. Further, the second electrode may be made of surface-passivated titanium, stainless steel, nickel, aluminum, or the like. Further, the second electrode may be made of a carbon structure such as graphite or a carbon nanotube, amorphous carbon, glassy carbon, or the like. Here, in view of durability, use of platinum, platinum black, platinum-oxide-coated platinum is more preferable.

In the invention, the first electrode and the second electrode are preferably plate-shaped, thin-film-shaped, mesh shaped, or fibrous. In particular, electrodes of [(2) paper-type fuel cell] and [(3) gel-type primary cell] according to embodiments of the present invention are preferably formed into a mesh shape which becomes a channel through which gas produced in the cells can be discharged. Here, "mesh shape" stands for a porous chamber in which through paths, through which gas to be discharged can pass, are

existent.

Specifically, as a mesh shaped electrode, the aforesaid electrode material may be made to adhere to a mesh made of metal, a punching metal plate, or a foamed metal sheet by a nonelectrolytic plating method, a vapor deposition method, or a sputtering method. Alternatively, the aforesaid electrode material may be made to adhere to paper made of cellulose or synthetic polymer by a similar method or a combination thereof.

Further, when the first electrode and the second electrode are disposed on both media including ion exchanging resins or ion conductive gels having high shape keeping ability, it is also a preferable aspect to dispose desired materials for electrodes on these ion exchanging resins or ion conductive gels by using a nonelectrolytic plating method, a vapor deposition method, or a sputtering method.

<Method of Power Generation>

A detailed description of a method of power generation (power generation mechanism) will be made.

The method of power generation comprises an acidic medium, a first electrode which is disposed in the acidic medium, a basic medium which is kept in contact with the acidic medium, and a second electrode which is disposed in the basic medium, wherein a first substance which is contained in the acidic medium causes a reaction of removing electrons from the first electrode, accompanied by hydrogen ions contained therein, and a second substance which is contained in the basic medium cause a reaction of donating electrons to the second electrode, accompanied by hydroxide ions contained therein.

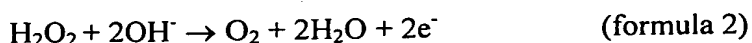
By this reaction, the first substance and the second substance undergo a chemical change into plural substances having a lower internal energy, and the energy for that amount is released to the outside as electric energy to generate electric power.

Further, here, an aspect will be explained in which the acidic medium is formed by an acidic aqueous solution, the basic medium is formed by the basic aqueous solution, and both the first substance and the second substance are hydrogen peroxide. However, although this is shown as the most preferable aspect of the present invention, the present invention is not limited to this.

The hydrogen peroxide produces water and oxygen by a decomposition reaction. When this chemical reaction is carried out by separating the reaction into an oxidation reaction and a reduction reaction at separate electrodes as in the cell of the invention, an electromotive force is generated. Namely, hydrogen peroxide, on the one hand, has an oxidizing function in an acidic reaction field and, on the other hand, has a reducing function in a basic reaction field, thereby generating an electromotive force. By using an acid-base bipolar reaction field such as this, the power generation method of the invention is realized.

More specifically, the power generation method of the invention will be described with reference to Fig. 1. Referring to Fig. 1, in the acidic reaction field (acidic medium) where the anode (first electrode) is disposed, hydrogen peroxide works as an oxidizing agent and, as shown below (formula 1), the oxygen atoms of hydrogen peroxide receive electrons from the electrode to produce water. Also, in the basic reaction field (basic medium) where the cathode (second electrode) is disposed, hydrogen peroxide works as a reducing agent and, as shown below (formula 2), the oxygen atoms of hydrogen peroxide

donate electrons to the electrode to produce oxygen and water. By these reactions, an electromotive force is generated, and power generated.



Further, in the reaction fields, the counter anion (corresponding to sulfate ion SO_4^{2-} in Fig. 1) of the hydrogen ion that is present in the acidic medium and the counter cation (corresponding to sodium ion Na^+ in Fig. 1) of the hydroxide ion that is present in the basic medium form a salt at the interface of the two media, whereby the balance of charge can be maintained. Since the salt formed at this time is usually more stable when ionized in an aqueous solution, the effect on the electromotive force by formation of the salt is far smaller than that on the electromotive force by the oxidation or reduction reaction at the electrodes. As a result of this, the bipolar-type cell of the invention in which the electrode reaction plays a principal role has a property of being capable of performing a more stable power generation than a different bipolar-type cell in which the neutralization reaction at the interface of the acidic and basic media plays a principal role.

An ion reaction formula obtained by summing up the half reaction formulas of (formula 1) and (formula 2) will be the following (formula 3).



According to the thermodynamic calculation, the enthalpy change (ΔH), the entropy change (ΔS), Gibbs free energy change (ΔG , temperature T : in units of Kelvin (K)) of this reaction will be respectively $\Delta H = -96.7\text{kJ/mol}$, $\Delta S = 18.9\text{J/Kmol}$, and $\Delta G = \Delta H - T\Delta S = -115.5\text{kJ/mol}$.

Also, the theoretical electromotive force (n is the electron number involved in the reaction, and F is a Faraday constant) and the theoretical maximum efficiency (η) can be calculated as $E = -\Delta G/nF = 1.2$ V, and $\eta = \Delta G/\Delta H \times 100 = 120$ %. A theoretical feature of this reaction is that the entropy increases due to the hydrogen peroxide decomposition reaction, whereby the sign of ΔS becomes positive. For this reason, the absolute value of ΔG will be larger than ΔH , so that the theoretical maximum efficiency exceeds 100 %. Being different from this, in the reactions of other fuel cells such as hydrogen-oxygen system or direct methanol system cells, the sign of ΔS becomes negative.

Based on the foregoing, the theoretical features in the case of using hydrogen peroxide as the first substance and the second substance in the power generation method of the invention will be described below.

In other fuel cells hitherto known in the art, the amount of entropy change $T\Delta S$, in principle, cannot be used for power generation and is released as heat. On the other hand, in the mechanism of the invention, the increase of the entropy obtained by absorbing heat from the outside can be used for power generation. Also, if the reaction temperature T is higher, the absolute value of ΔG will be larger, thereby raising the electromotive force.

In a practical cell, the output voltage is determined not solely by the theoretical electromotive force of the ion reaction formula. Overvoltage or the like causes decrease of the voltage and simultaneously generates heat. For example, when unit cells are stacked for integration, or in incorporating the cell into a commercial product, this heat will be a great problem. However, as described above, according to the power generation method of the invention, the heat can be theoretically reused for power generation, raising a

possibility that the total heat generation will be smaller. Further, ΔG corresponding to the total amount of energy that can be used for power generation is about half the energy generated by hydrogen/oxygen fuel cells. However, since $n=1$ ($n=2$ in the case of hydrogen-oxygen fuel cells), ΔG will have the same amount of the theoretical electromotive force.

In view of the aforementioned, in the cell of the present invention and in the method of power generation of the present invention, when hydrogen peroxide is used for the first substance and the second substance, the effects described below can be obtained:

- (1) Hydrogen peroxide does not discharge carbon dioxide, and instead, discharges oxygen in accordance with the reaction for converting chemical energy into electric energy. Further, since flammable and combustible materials or harmful heavy metals are not used for structural components in the cells, hydrogen peroxide is excellent in environmental safety over the entire life cycle of manufacturing, consumption, and discharging processes.
- (2) Since hydrogen peroxide is in a liquid state at an ordinary temperature and under a normal pressure, heavy metal cylinder or the like for storing hydrogen peroxide becomes unnecessary. Besides, hydrogen peroxide can be mixed freely with water, and gelated easily. Accordingly, it is possible to use a fuel supply method having excellent storage properties and portability.
- (3) Use of oxygen as an oxidizing agent becomes unnecessary thereby facilitating hydrogen peroxide to be used without being hindered when hydrogen peroxide is used under a closed environment in which the amount of air is limited or under a critical environment in which the content of dust or waste in the air is relatively large.

(4) As the industrial manufacturing method of hydrogen peroxide, an organic method is already established such that anthraquinone is used as an intermediate (which is reused repeatedly without being consumed) to synthesize hydrogen peroxide by conducting a contact-reduction of hydrogen using a catalyst and an air oxidization. In status quo, hydrogen peroxide is supplied stably and inexpensively. In addition, hydrogen peroxide is able to form a part of a cell with a simple structure by using less peripheral parts, whereby the entire weight and the volume of the whole cell system can be minimized. Accordingly, cells with high durability can be manufactured inexpensively.

In the above-description, a description of a method of power generation using hydrogen peroxide as the first substance and the second substance has been made. However, when other substances (compounds) are used for both substances, they are substantially common in points that oxidation and reduction reactions are caused to provoke at the electrodes

Therefore, according to the cell of the invention and the power generation method of the invention, stable power generation is enabled owing to the power generation mechanism thereof.

Further, in the cell of the invention and in the method of power generation of the invention, a product which is produced due to the reaction of electrodes is produced not between the electrodes but in the vicinity thereof. Accordingly, when the removal of the product is required, it can be removed easily from the outside of a box member containing therein a cell structure. Further, if the product produced by the reaction between the electrodes is water, and the acidic medium or the basic medium is an aqueous solution, or if

the first substance and the second substance are used by being mixed with an aqueous solution, dissolved, and dispersed, the produced water can be easily removed from portions near the electrodes by being dispersed into both media or by being discharged to the outside of the cell.

75/ Hereinafter, a description of a preferable embodiment of the cells of the present invention will be made. However, the present invention is not limited to this. Preferable examples of the cells of the present invention include (1) chip-type fluid fuel cells, (2) paper-type fuel cells, and (3) gel-type primary cells.

[(1) Chip-type fluid fuel cell]

This chip-type fluid fuel cell has an acid-basic bipolar reaction field. In the reaction field, a liquid such as a sulfuric acid aqueous solution is used as the acidic medium and a liquid such as a sodium hydroxide aqueous solution is used as the basic medium. With reference to Fig. 2, a description of a specific structure of the cell will be made.

Fig. 2A is a schematic perspective view of a top surface of a chip-type fluid fuel cell. As shown in this figure, the chip-type fluid fuel cell has a capillary channel 1 (having a depth of 50 μ m and a width of 1000 μ m). The capillary channel 1 is formed between a slide glass 11 and a cover glass 10 through a spacer (member 12 in Fig. 2B). The capillary channel 1 is provided with inlets 2 and 3 for supplying a liquid state acidic medium in a liquid state and a liquid state basic medium, and outlets 4 and 5 for discharging these therefrom. For example, when an acidic aqueous solution "a" from the inlet 2 and a basic aqueous solution "b" from the inlet 3 are flown into the capillary channel

1, when appropriate viscosity and flow rate are provided for the liquids, laminar flow (Reynolds flow) is formed at a junction portion of the capillary channel 1.

With reference to Fig. 2B, laminar flows will be explained. Fig. 2B shows a cross-sectional view of the chip-type fluid fuel cell which is taken along a line A-A', as seen from directions in which both media flow. As shown in this figure, the acidic aqueous solution "a" and the basic aqueous solution "b" form laminar flow "a" and laminar flow "b", respectively, even at the junction portion of the capillary channel 1. Although the solutions "a" and "b" are kept into contact with each other, they are flown through the capillary channel 1 without crossing each other. Then, while the solutions "a" and "b" are passed through the junction portion, they still form the laminar flows "a" and "b" continuously. Next, they are separated again at a branch portion. The solution "a" is discharged from the outlet 4, and the solution "b" is discharged from the outlet 5, and collected separately.

Two platinum electrodes 6 and 8 are formed at the bottom of the junction portion of the capillary channel 1 for forming such laminar flows as described above. Electric power can be taken to the outside, through each of connecting terminals 7 and 9.

In this way, a state in which two liquids, which are kept into contact with each other, form laminar flows without being mixed with each other can be implemented by applying a viscous fluid property to the capillary channel. The viscous fluid property stands for a phenomenon (Reynolds phenomenon) occurring when Reynolds number (Re) of constants which are determined in accordance with the configuration of the channel (e.g., tube diameter or width or depth of one channel) is about 2000 or less. By using the

phenomenon, two liquids having appropriate viscosity and moving speed form laminar flows in the capillary, and a property is exerted in which the mixture of two liquids hardly occurs. For this reason, in a state in which the first substance and the second substance are made to coexist in both laminar flows, when electrodes are put in the laminar flows, oxidation reaction is provoked in the acidic medium and the reduction reaction is provoked in the basic medium, and an electromotive force is generated, and a cell is formed.

When this chip-type fluid fuel cell is considered as a single unit cell, by arranging plural unit cells in parallel or in series, the amount of current and that of voltage are increased. The complicated structure of the capillary channel can be easily formed by applying ultrasonic waving grinding or semiconductor photolithography, and existing processing technologies such as sandblast, injection molding and silicon resin molding, to substrates (chips) such as glass, quartz, silicon, polymer film, a plastic resin, ceramics, graphite, metal and the like. Accordingly, integration of unit cells and lamination of plural chips make it possible to construct a cell system with desirable performances (in currents and voltages).

[(2) Paper-type fuel cell]

A paper-type fuel cell has an acid-base bipolar reaction field in which a solid state acidic medium and a solid state basic medium are kept into contact with each other, and disposed. With reference to Figs. 3A and 3B showing a schematic cross-sectional perspective view of a paper-type fuel cell, a description of a specific structure thereof will be made.

The paper-type fuel cell shown in Fig. 3A has a structure in which an acidic reaction field having the first electrode 22 and an acidic medium 20 and a basic reaction field having the second electrode 32 and a basic medium 30 are kept into contact with each other. The first substance and the second substance are supplied into the cell, so that power is generated. For example, when the first substance and the second substance are hydrogen peroxide, an aqueous solution "L" of hydrogen peroxide is dripped or soaked, and supplied into the cell as indicated by an arrow in Fig. 3A. Accordingly, oxidation reaction in the acidic reaction field and reduction reaction in the basic reaction field are provoked, so that an electromotive force is generated. Further, the configuration of an electrode is preferably formed into a mesh shape which becomes a channel through which gas produced in the cell can be discharged.

Further, the paper-type fuel cell in Fig. 3A is structured in accordance with an aspect in which the method of supplying the aqueous solution of hydrogen peroxide in Fig. 3B has been modified. In other words, a supplying member 40 having a fabric or capillary member by which the solution can be soaked or absorbed is provided at a portion of the interface between the acidic medium 20 and the basic medium 30, and through the supplying member 40, the solution can be supplied into the acidic medium 20 and the basic medium 30. Accordingly, oxidation reaction in the acidic reaction field and reduction reaction in the basic reaction field are provoked, and an electromotive force is generated. Also at this point, the electrode is preferably formed into a mesh shape which becomes a channel through which gas produced in the cell can be discharged.

As described above, preferable examples of the acidic medium 20 and the basic

medium 30 include: a combination of a matrix containing a strong acid substituent group (such as a sulfuric acid group or a phosphoric acid group) with a matrix containing a strong basic substituent group (such as a quaternary ammonium group); a combination of a strong acidic ion exchange resin with a strong basic ion exchange resin; a combination of a strong acidic ion exchange filter paper with a strong basic ion exchange filter paper; and a combination of a solid super strong acid with a solid super strong base.

Water is decomposed into hydrogen ions and hydroxide ions, and supplied at a contact-interface of the acid-base bipolar reaction field in the above-described paper-type fuel cell. Then, the solution of hydrogen peroxide from the outside is supplied into the reaction field, whereby electric power can be supplied continuously. Further, in the cell, the solution of hydrogen peroxide is supplied by means of dripping or soaking, so that the cell has an advantage that the solution is supplied without using external pumps.

Moreover, the cell can also make use of a phenomenon in which water as the reaction product is transpired from the surface of the cell into the atmosphere.

[(3) Gel-type primary cell]

A gel-type primary cell has an acid-base bipolar reaction field in which an ion conductive gel due to a gelation of an acidic aqueous solution as an acidic medium and an ion conductive gel due to a gelation of a basic aqueous solution as a basic medium are kept into contact with each other, and disposed. With reference to Fig. 4 showing a schematic cross-sectional perspective view of a gel-type primary cell, a description of a specific structure thereof will be made.

The gel-type primary cell shown in Fig. 4 has a structure in which an acidic reaction field comprising a first electrode 22 and the acidic medium 20, and a basic reaction field comprising a second electrode 32 and the basic medium 30 are kept into contact with each other, and the acidic medium 20 contains the first substance, and the basic medium 30 contains the second substance. For example, when the first substance and the second substance are hydrogen peroxide, an aqueous solution of hydrogen peroxide is made coexistent in the acidic medium 20 or the basic medium 30 or in both media. Accordingly, oxidation reaction in the acidic reaction field and reduction reaction in the basic reaction field are provoked, and an electromotive force is generated. Moreover, the electrode is preferably kept into contact with the media at one side or both sides thereof, and preferably formed into a mesh shape which becomes a channel through which gas produced in the cell can be discharged.

In accordance with power generation of the gel-type primary cell, at the time when hydrogen ions or hydroxide ions or the aqueous solution of hydrogen peroxide contained in the electronic conductive gel are consumed (salt is generated simultaneously), and used up, the supply of electric power is stopped. Further, these substances to be consumed cannot be re-supplied from the outside, so that they are used for manufacturing primary cells. However, the cell is not only simply structured but also makes use of a gel state having high self-maintenance for both reaction fields. Consequently, the reaction fields can be maintained stable thus making it possible to take a seal-state cell formation which is excellent in portability and cost performance.

As described above, a description of the cell according to the embodiments of the

present invention has been made. However, the structure of the present invention is not limited to this. For example, the cell having the above-described structure and conventional cells using hydrogen fuel or methanol fuel are used in combination as a composite generator.

EXAMPLES

Hereafter, the effect of the present invention will be described by way of Examples and Comparative Example. However, the invention is not limited to these.

[Example 1]

The chip-type fluid fuel cell shown in Fig. 2 was evaluated by undergoing an experiment of power generation under the following conditions and by determining current-voltage properties.

Namely, a 3 wt. % of an aqueous solution of hydrogen peroxide which is commercially available (NIPPON YAKKYOKU HO "OXYDOL", produced by Kenei Pharmaceutical Co., Ltd.) was mixed with sulfuric acid (96% of guaranteed substance, produced by KANTO CHEMICAL CO., INC.) and distilled water, and a sample liquid A (0.75mol /l of hydrogen peroxide and 0.75N (1.5mol/l) of sulfuric acid) was prepared. Further, the solution was mixed with sodium hydroxide (97% of guaranteed substance, produced by KANTO CHEMICAL CO., INC.) and distilled water, and a sample liquid B (0.75mol/l of hydrogen peroxide and 0.75N (1.5mol/l) of sodium hydroxide) was prepared.

Thereafter, the sample solution A and the sample solution B were pumped by an

external pump and injected into the inlet 2 and the inlet 3 of the chip-type fluid fuel cell, respectively. The flow rates of both sample liquids were $24\mu\text{l}/\text{sec}$ (Re: Reynolds number is about 670) at the central portion of each channel, and the experiment temperature was at a room temperature. Generation of gas was not observed on the surface of an electrode 8 (platinum thin film, area size: 0.026 cm^2), which is kept into contact with the sample liquid A, at the bottom of the channel. Meanwhile, generation of gas was observed on the surface of an electrode 6 (platinum thin film with an area of 0.026 cm^2), which is kept into contact with the sample liquid B, at the bottom of the channel. This is because the electrode 8 behaved as an anode when water was produced due to the reaction in Formula 1, and the electrode 6 behaved as a cathode when oxygen and water were produced due to the reaction in Formula 2.

Current-voltage properties obtained by the fuel cell under the aforementioned experimental conditions are shown in Fig. 5. The cell in Example 1 had a release voltage of 700 mV and a maximum output of $23\text{mW}/\text{cm}^2$ (when the electromotive voltage is 300mV and the current is $77\text{mA}/\text{cm}^2$).

[Example 2]

A chip-type fluid fuel cell which is the same as that in Example 1 was used and evaluated in the same manner as in Example 1 except that the concentration of hydrogen peroxide contained in the sample liquids was changed. Further, the concentration of hydrogen peroxide in both sample liquids A and B which were injected into the inlets 2 and 3 of the chip-type fluid fuel cell was 0.45 mol/l . Moreover, the flow rate and the

experimental temperature were the same as those in Example 1.

Current-voltage properties which were obtained by using fuel cells under such experimental conditions are shown in Fig. 5. The cell in Example 2 had a release voltage of 675 mV, and a maximum output of 9 mW/cm².

[Example 3]

A chip-type fluid fuel cell which is the same as that in Example 1 was used and evaluated in the same manner as in Example 1 except that the concentration of hydrogen peroxide contained in the sample liquids was changed. The concentration of hydrogen peroxide of both sample liquids A and B which were injected into the inlets 2 and 3 of the chip-type fluid fuel cell was 0.22 mol/l. Moreover, the flow rate and the experimental temperature were the same as those in Example 1.

Current-voltage properties which were obtained by using fuel cells under such experimental conditions are shown in Fig. 5. The cell in Example 3 had a release voltage of 620 mV, and a maximum output of 3 mW/cm².

[Example 4]

A chip-type fluid fuel cell which is the same as that in Example 1 was used and evaluated in the same manner as in Example 1 except that the concentration of hydrogen peroxide contained in the sample liquids was changed. Further, the concentration of hydrogen peroxide of both sample liquids A and B which were injected into the inlets 2 and 3 of the chip-type fluid fuel cell was 0.10 mol/l. Moreover, the flow rate and the

experimental temperature were the same as those in Example 1.

Current-voltage properties which were obtained by using fuel cells under such experimental conditions are shown in Fig. 5. The cell in Example 4 had a release voltage of 611 mV and a maximum output of 1 mW/cm².

[Example 5]

A chip-type fluid fuel cell which is the same as that in Example 1 was used and evaluated in the same manner as in Example 1 except that materials used for the first electrode and the second electrode were changed as follows, and the concentration of hydrogen peroxide contained in the sample liquids were changed. The material for the electrode 6 was changed to silver, and that for the electrode 8 was changed to platinum. Further, the concentration of hydrogen peroxide of both sample liquids A and B which were injected into the inlets 2 and 3 of the chip-type fluid fuel cell was 0.45 mol/l. Moreover, the flow rate and the experimental temperature were the same as those in Example 1.

On the basis of current-voltage properties which were obtained by using fuel cells under such experimental conditions, the cell in Example 5 had a release voltage of 540 mV and a maximum output of 6 mW/cm².

[Example 6]

In the paper-type fluid fuel cell shown in Fig. 3A, the cell was evaluated by undergoing an experiment of power generation under the following conditions and by

determining current-voltage properties.

The acidic medium 20 used a small piece (height: 1.5 cm × width: 1.5 cm) of strong acid ion exchange filtrate paper (RX-1 SERIES CP-1, produced by TORAY CHEMICAL CO., LTD.), and the basic medium 30 used a small piece (height: 1.5 cm × width: 1.5 cm) of strong acid ion exchange filtrate paper (RX-1 SERIES AP-1, produced by TORAY CHEMICAL CO., LTD.). Further, the first electrode 22 and the second electrode 32 were formed by adhering to the acidic medium and the basic medium, respectively, platinum black mesh (nickel mesh surface having 100 meshes was black-platinized) having the same area as each of the acidic medium and the basic medium.

Then, as indicated by an arrow in Fig. 3A, the first substance and the second substance were supplied into the cell by dripping a 3 wt.% aqueous solution of hydrogen peroxide L (NIPPON YAKKYOKU HO "OXYDOL", produced by Kenei Pharmaceutical Co., Ltd.). Accordingly, oxidation reaction in the acidic medium and reduction reaction in the basic medium were provoked, and an electromotive force was generated.

Current-voltage properties which were obtained by using fuel cells under such experimental conditions are shown in Fig. 6. The cell in this example exerted a release voltage of 120 mV and a maximum output of $0.35 \mu\text{W}/\text{cm}^2$ (when an electromotive voltage is 80 mV and current is $0.01 \text{ mA}/\text{cm}^2$).

[Example 7]

In the gel-type primary cell shown in Fig. 4, the cell was evaluated by undergoing an experiment of power generation under the following conditions and by determining

current-voltage properties.

The acidic medium 20 (that in which 0.25 mol/l of sulfuric acid and 0.5 mol/l of hydrogen peroxide were gelated with 10 wt/% of anhydrous silicon dioxide) and the basic medium 30 (that in which 0.5 mol/l of sodium hydroxide and 0.5 mol/l of hydrogen peroxide were gelated with 8 wt. % of crosslinked sodium polyacrylate) were used. Platinum black mesh (nickel mesh surface having 100 meshes was black-platinized) having an area of 2.6 cm² was adhered to each of the media, and used as the first electrode 22 and the second electrode 32.

On the basis of current-voltage properties which were obtained by using the primary cell under such experimental conditions, the cell in Example 7 had a release voltage of 570 mV and a maximum output of 0.2 mW/cm² (when an electromotive voltage is 30 mV and current is 1.7 mA/cm²).

[Comparative Example 1]

A chip-type fluid fuel cell which is the same as that in Example 1 was used and evaluated in the same manner as in Example 1 except that hydrogen peroxide was not contained in the sample liquids, and the concentration of sulfuric acid and sodium hydroxide were changed. The concentrations of both sulfuric acid and sodium hydroxide of the sample liquids A and B, which were injected into the inlets 2 and 3 of the chip-type fluid fuel cell, were 0.45 mol/l. Moreover, the flow rate and the experimental temperature were the same as those in Example 1.

Current-voltage properties which were obtained by using fuel cells under such

experimental conditions are shown in Fig. 5. In Comparative Example 1, although a release power (300 mV) due to a voltage between liquids was measured, a significant current was not flown.

As described above, in accordance with Examples, voltages and currents were obtained as shown in Figs. 5 and 6, and voltages and currents were obtained in Examples 5 and 7. Therefore, it has been found out that power generation is carried out, and electric energy can be supplied by using a cell having a novel structure and a method of power generation using the cell according to the present invention.

Industrial Applicability

The cell according to the invention is a bipolar-type cell having a novel structure, and its main source is an electromotive force which is generated due to oxidation and reduction reactions at electrodes as solid matters. Therefore, stable power generation is enabled. Various problems with the conventional cells are solved by the cell and the method of power generation using the cell according to the present invention.

Accordingly, the following advantages can be provided by the present invention. In other words, occurrence of danger during the use of flammable and ignitable fuels can be solved, discharge of carbon dioxide is prevented, and storage properties of the cell are simple, and the structure of the cell is simple. As a result, industrial applicability of the present invention is extremely high.